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**THE DETERMINATION OF CELLULOSE
IN WOOD**

BY

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THESIS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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ENTITLED The Determination of Cellulose In Wood

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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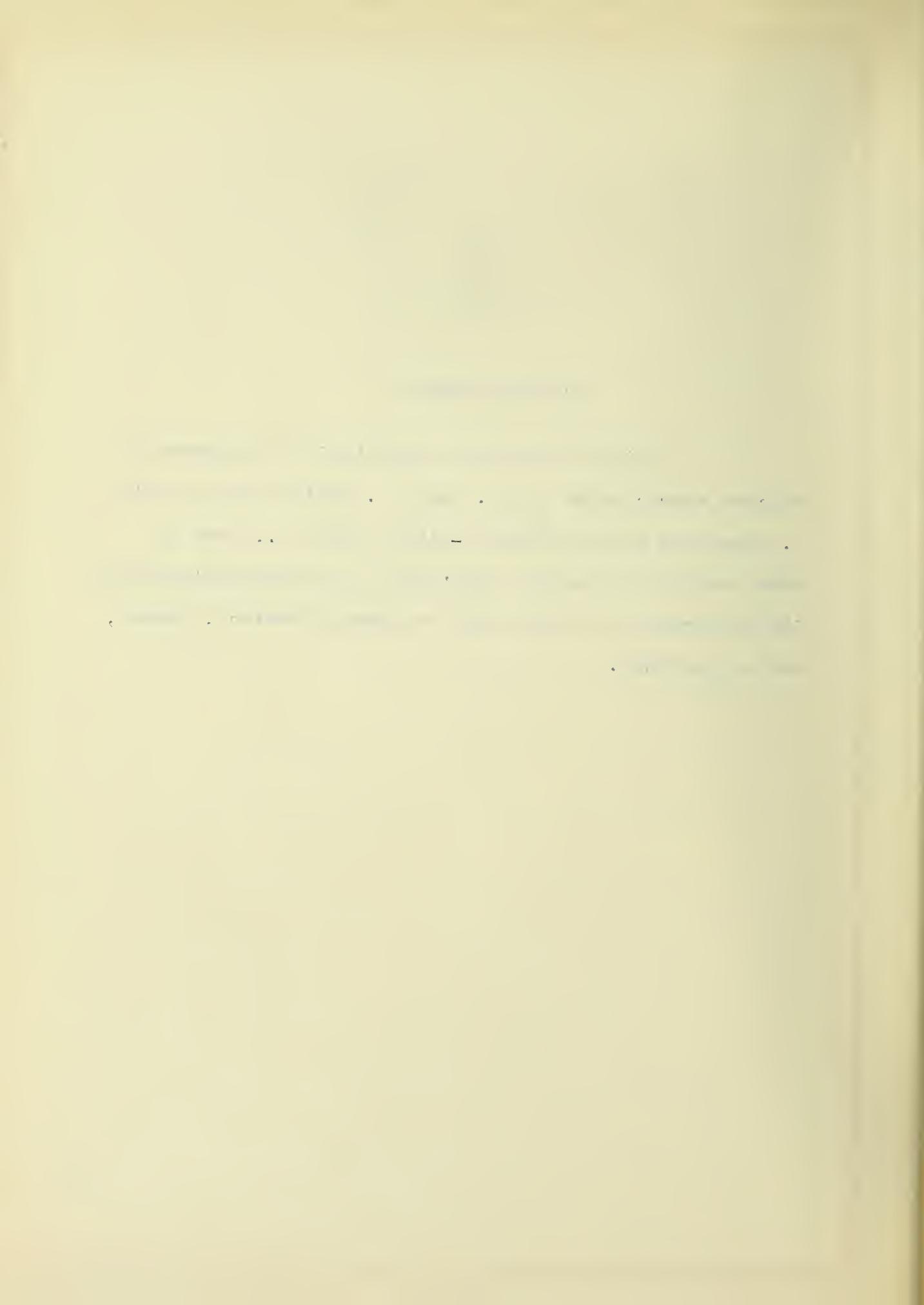
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INTRODUCTION

The determination of cellulose in wood has been the subject of considerable discussion and research in the past twenty-five years, but it was only during the last few years that the need of a more accurate and rapid^{method} was felt. This need was experienced by pulp and paper mill chemists where the cellulose content in the raw materials is a determining factor in the quality of the product. Although the yield of pure cellulose fiber never reaches its theoretical value in the manufacture of pulp and paper because of the hydrolytic and oxidizing effects of the reagents used, this cellulose value enables the paper maker to see how nearly his process is approaching the optimum. Because of this urgent need, mill chemists and investigators have set to work to find out if the former standard methods could be improved or new ones discovered. Almost every mill at present uses its own method which is usually some standard method which has been modified to suit the technique of the operator.

Historical and Theoretical

Because of the meagerness of knowledge in the field of wood chemistry, the uncertainty that exists as to what constitutes wood cellulose, and the great variety of methods employed in determining the cellulose in wood - none of which give accurate results that can be checked by different operators, it seems to be appropriate at this time to give a resume of the work that has been done in an endeavor to discover a method that will render results of cellulose determinations in wood both accurate and comparable.

Cross and Bevan, in their book on "Researches on Cellulose 1895 - 1900", discuss briefly the methods in use at that time and come to the conclusion that the method of Schulze - prolonged digestion with nitric acid with the addition of chlorate - gave the nearest approximation of "actual cellulose" in the raw material. They do not recommend their own method, which is used quite extensively at the present time, because the product formed yielded 9% of furfural on distillation with HCl, showing that the process resulted in a substance that was not pure normal cellulose. Most of the methods discussed in Cross and Bevan's book consist of acid or alkaline treatment of the wood, yielding a more or less complex mixture of celluloses and furfureoids.

Sutermeister (1), in a more recent book, reviews some of Renker's work on methods of determining cellulose (2). Renker concludes, after a large number of experiments with different methods, "that there is absolutely no correct method for determining the cellulose in woods but that the method of Cross and Bevan is the

most satisfactory". Other investigators (Konig and Hohn) do not approve of this process and claim that only hydrolysis followed by oxidation can free the true cellulose from all impurities. Heuser and Sieber (3), on the contrary, proved that lignin can be completely removed by chlorination without any oxidation of the cellulose; that is, cellulose will not be oxidized by the chlorine until all of the lignin has been removed and this stage of the process can easily be detected because of the characteristic color produced by sodium sulphite solution on lignin chloride.

Although Cross and Bevan's method is used more extensively than any others, there are many particulars in the procedure that render the results of different operators unfit for comparison. Their original method involved a preliminary hydrolysis with 1% NaOH, but at the present time there is considerable doubt as to whether that preliminary treatment is necessary or not. Dore (4), after experimenting with three proposed methods for treating woods previous to chlorination, comes to the conclusion that "all methods processes involving preliminary hydrolysis, either acid or alkaline, result in a diminished yield of both α and total cellulose". This method, however, has been severely criticised because of the high furfural yield of the residue which, according to some investigators, can be removed by hydrolysis with dilute inorganic acids. Again this hydrolytic treatment has been criticised by Johnsen (5) who has shown that, although furfural yielding compounds are subject to hydrolysis, normal cellulose is also attacked by dilute inorganic acids. After Schwalbe and Johnsen (6) found that cellulose heated with a mixture of glycerol and acetic acid did not show any signs

of attack, Hovey and Johnsen proposed a method (7) consisting of a four hour hydrolysis with glycerol and acetic acid at 135 C, followed by the subsequent chlorination. This method proved to yield a residue of high purity because, according to Johnsen, the acetic acid-glycerol mixture is able to hydrolyze lower carbohydrates and the greater portion of the furfural yielding substances without attacking the cellulose itself. Mahood, on the contrary, shows by means of convincing experimental data(8) that the yield of pentosan-free cellulose as well as the pentosan content of the cellulose is reduced by preliminary treatment with the acetic acid-glycerol mixture. Then if the definition of wood cellulose is accepted as being the residue remaining after successive alternate treatments with chlorine and dilute Na_2SO_3 solution until free from lignin derivatives, the residue consisting of hexosans, pentosans, and possibly furfural yielding compounds other than pentosans, this method involving hydrolysis with glycerol and acetic acid certainly does not give a true value for wood cellulose.

It is very evident from the literature on the subject that nothing definite has been decided upon as to the preliminary treatment primarily because all investigators do not know and do agree as to what constitutes wood cellulose. Dore (4) submits a definition of wood cellulose as being the residue remaining after successive alternate treatments with chlorine and Na_2SO_3 solution until free from lignin. Wise and Russell state (12), after a careful survey of the results on wood cellulose chemistry, that the term would better be defined as being the residue after such a treatment with a correction applied for the pentosan and methyl pentosan

content of the residue. It is an established fact that the residue is not the same as cotton cellulose but, in attempting to clear up the confusion that exists as to what constitutes wood cellulose, Wise and Russell (12) have verified the conclusions of other investigators that the normal cellulose of wood is the same as that of cotton. Only after the exact composition of this so-called wood cellulose is known can a method for determining the cellulose in wood be proposed and accepted. Until such facts are known, industries using such determinations must make the best of the methods known at the present time.

Considerable work has been done to determine the best length of period of chlorination for the wood fiber. In Cross and Bevan's original method (11), an initial chlorination period of one hour was recommended, but at the present time it is a recognized fact that one hour is too long; consequently their method has been modified to suit different operators. Schorger, during his extensive work on the "Chemistry of Wood" (9), used one-half hour chlorination periods or fractions thereof until the residue gave no lignin reaction. Dore (4) used periods of exposure to chlorine as being 20 - 15 - 15 - 10 minutes respectively. Mahood (8) found that five one-half hour chlorinations were required for complete reduction following Cross and Bevan's procedure. Renker (5) obtained from wood a residue that did not give any lignin reactions by repeating the chlorination six times with a total exposure to the gas of 2.75 hours. He also concludes from his experiments that periods of chlorination should be as short as possible. Sieber and Walter (5) found that four chlorinations with a total exposure of one hour were

sufficient to remove all of the lignin from the wood without injury to the cellulose.

Whatever the time for exposure, the chlorination in each case was followed by a thorough solution of the lignin derivatives with Na_2SO_3 solution. Although the periods of chlorination differ considerably in each case, it was agreed by all investigators that the length of the periods should be as short as possible, depending on the physical state of the sample and on the type of wood.

In addition to the different opinions as to the nature of the preliminary treatment, if any at all, and the length of period of exposure to chlorine, methods differ widely as to the type of apparatus in which the chlorination takes place. Schorger (9) used an apparatus consisting of a jar with an inlet and an outlet for water and fitted with a removable lid. Into this jar were placed four beakers containing the sample of sawdust. The chlorine was allowed to flow into the beaker through tubes which were fitted with stop cocks and terminated in one main line outside of the jar. Dore, in his work on the "Determination of Cellulose in Woods" (4), used the Sieber and Walter method with a unique type of apparatus. The material was contained in a Gooch crucible connected with a filter flask. A glass adapter capped over the filtration tube and connected to the chlorine generator. Later Dore proposed a vacuum method (10) in which the sample was introduced into a wide mouthed bottle or flask, the flask evacuated, and the sample saturated with chlorine. Johnsen and Hovey (7) suggested the use of a Gooch crucible fitted with a calico filter pad - the sample remaining in the cru-

cible throughout the procedure. Cross and Bevan's method as reviewed by Dean and Tower (11), was to wash the fiber on a cloth or wire, squeezed to remove the excess water, and then placed in a beaker into which a stream of chlorine was passed. These same investigators, after experimenting with many types of apparatus, adopted that of a small perforated porcelain filter plate in a five inch funnel. With this it was necessary to filter several times before a clear filtrate was obtained.

Many investigators claim that an apparatus that allows the fiber to remain in the crucible or beaker throughout the operation is the best. This may be true but there are several disadvantages of such types in that the fiber mats down tightly and does not allow the chlorine to reach all of the particles. Then, too, with a little practice, an operator can handle an apparatus efficiently that does involve several transfers of material.

There is one particular in Cross and Bevan's method that has not received as much attention as others but seems to be no less important. That is the physical state of the wood during chlorination. Cross and Bevan merely stated in their original procedure that the wood must be reduced to the "finest possible shavings". In the method adopted by Dean and Tower (11) wood that sifted through a screen having 24 meshes to the inch was used. Schorger used the material in two different forms (9) - sawdust and shavings not more than 0.005 mm. in thickness. These shavings were screened and all that passed through a 40 mesh screen was rejected. The sawdust was ground to pass through a 40 mesh screen. Johnsen and Hovey (7) find

that, in order to reduce the time of chlorination to a minimum, the material should be of such fineness and uniformity as to pass through an 80 mesh screen but be retained on a 100 mesh screen, Dore(10) used material that passed through a 2 mm. sieve. In a more recent paper, Dore (4) obtained a sample of sawdust by sifting it through a 50 mesh screen. Mahood conducted an extensive study on the "Effect of Size of Particle on the Yield of Cellulose" (8) and comes to the conclusion that material which passes through an 80 mesh sieve but is retained on a 100 mesh screen is the most satisfactory for cellulose determinations. This material is not representative of the entire sample so he recommends the combination of two forms, those from sawing and grinding. He also concludes that the variation in cellulose content using various sizes of particles is due to:

1. Too wide a range in size of particle in the material causing an attack on the cellulose of the smaller particles before the non-cellulose material of the larger particles can be removed.
2. A possible fractionation of the materials due to sifting out certain portions.

It is quite evident from the experimental data of several investigators that the material of this type is the most satisfactory but certainly is not representative. Table 1 shows the proportion of different meshes in a 100 gram sample of White Spruce sawdust obtained by means of a woodworker's rasp.

Table 1.

100 mesh	2.4%
80 "	2.4%
60 "	10.60%
40 "	41.8%
20 "	42.8%

It is obvious from this data that to take the 80 mesh portion which is only 2.4% of the entire sample as being representative of the sample is a decided error. One way of overcoming this difficulty is to grind the sawdust so that a larger portion of the sample will pass through the 80 mesh sieve. As yet no grinding apparatus is available that will give such a sample. Another alternative is to work out an analytical procedure that will give consistent results on all meshes from 20 to 100 since this range includes the major portion of the sample.

Object of the Investigation. It is the object of this research to study the effect of size of particle on the yield of cellulose from wood and from the data obtained, attempt to formulate a procedure that can be adapted to any size of sawdust between 20 and 100 mesh.

Experimental

Method. The method used in this work is that of Cross and Bevan which has been modified by the operators at the Kimberly-Clark Paper Co.

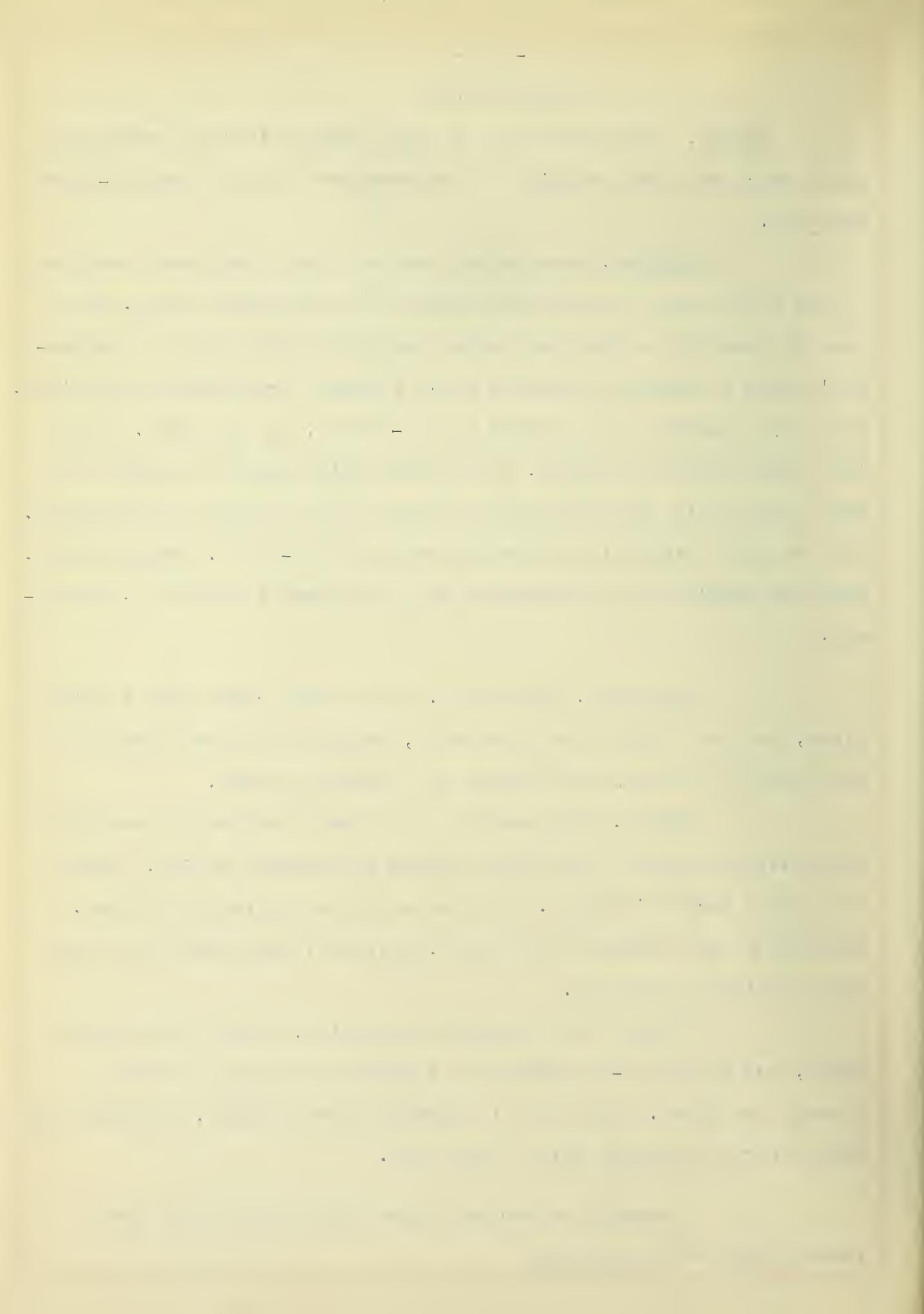
Sampling. Samples are best obtained from green wood but if the wood is dry it should be soaked in water before using. The wood is placed in a vise and rasped across the grain with a woodworker's rasp to obtain the sample in as fibrous a condition as possible. The entire sample is then dried at 98 - 100 C. for one hour. It is then quartered and screened, the portion which passes through a 48 mesh wire and is retained on an 80 mesh wire is taken as the sample*. This is again placed in the drying oven at 100 - 105 C. for two hours. One gram samples are then weighed out and placed in a 500 cc. casserole.

Procedure. Add 200 cc. of 1% NaOH, cover with a watch glass, and boil gently for 30 minutes, washing the fiber down from the sides of the dish and keeping the volume constant.

Filter, with suction, on a small perforated porcelain plate covered on both sides with pieces of bleached calico, placed in a 2 1/2 inch 60' funnel. Refilter until the filtrate is clear. Wash with a good volume of hot water, suck dry, and loosen the fiber with a pointed glass rod.

Attach to the chlorine generator, cover with a watch glass, and allow 60 - 70 bubbles of chlorine per minute to pass through the fiber. Allow this to continue for one hour, loosening the fiber every 15 minutes with a glass rod.

* Samples of various sizes were used in this work varying from 10 to 100 mesh.



After chlorination, remove the funnel to a filter flask and wash with hot water to remove the HCl formed during chlorination.

Transfer the fibers from the funnel to a 500 cc. casserole by means of a wash bottle filled with 150 cc. of 3% Na₂SO₃. Add the remaining amount of Na₂SO₃, place on a hot plate, and bring to a boil. Add 3 cc. of 10% NaOH and boil for 5 minutes

Again collect the fibers on the filter plate, wash with hot water until the dark color is removed, suck dry, and loosen the fiber with a glass rod.

Expose to chlorine as before but this time for only 30 minutes. Repeat the Na₂SO₃ treatment.

Repeat the chlorination until the fiber turns white on being exposed to the gas. This should happen after the third exposure (15 minutes).

However, at which stage of the operation this does take place, remove from the generator, and wash with a large volume of hot water. Transfer to a casserole and allow it to stand under hot water for 15 minutes.

Collect in a tared Gooch crucible, provided with a calico filter pad, wash with hot water, then with 25 cc. of alcohol and finally with the same amount of ether. Dry at 105 C. for two hours and weigh.

If the fiber is not washed well at all times, the final residue will have a dirty brown color. This takes place no matter how white the fiber is before drying.

The greatest error in any method of this type occurs in transferring the fiber from one container to another but with special care and attention on the part of the operator this error

can be practically eliminated.

Results. The results of determinations on White Spruce, Balsam, Poplar, and Hemlock are compiled in Table 2.

Degree of mesh	White Spruce	Balsam	Poplar	Hemlock
8	57.70 58.17			
10		51.78 51.07	56.60 55.72	55.95 54.99
14	57.48 56.66			
20	56.33 56.83	49.63 49.87	60.03 58.20	55.81 54.41
28	54.75 55.48			
40		48.14 48.69	56.55 57.48	54.95 57.56
48	52.18 52.38			
60		47.11 47.01	55.43 56.00	50.40 54.09
80	51.07 50.88	46.30 46.51	54.65 54.43	51.31 47.21
100	50.16 50.98	45.38 45.70	54.28 54.56	50.38 50.86

Conclusions and Discussion

Samples of 8, 14, 28, and 48 mesh were used with the White Spruce and not with the others because the sample of Spruce was prepared at the Kimberly-Clark Paper Co., while the others were prepared at the laboratory at school.

Curve 1
White Spruce

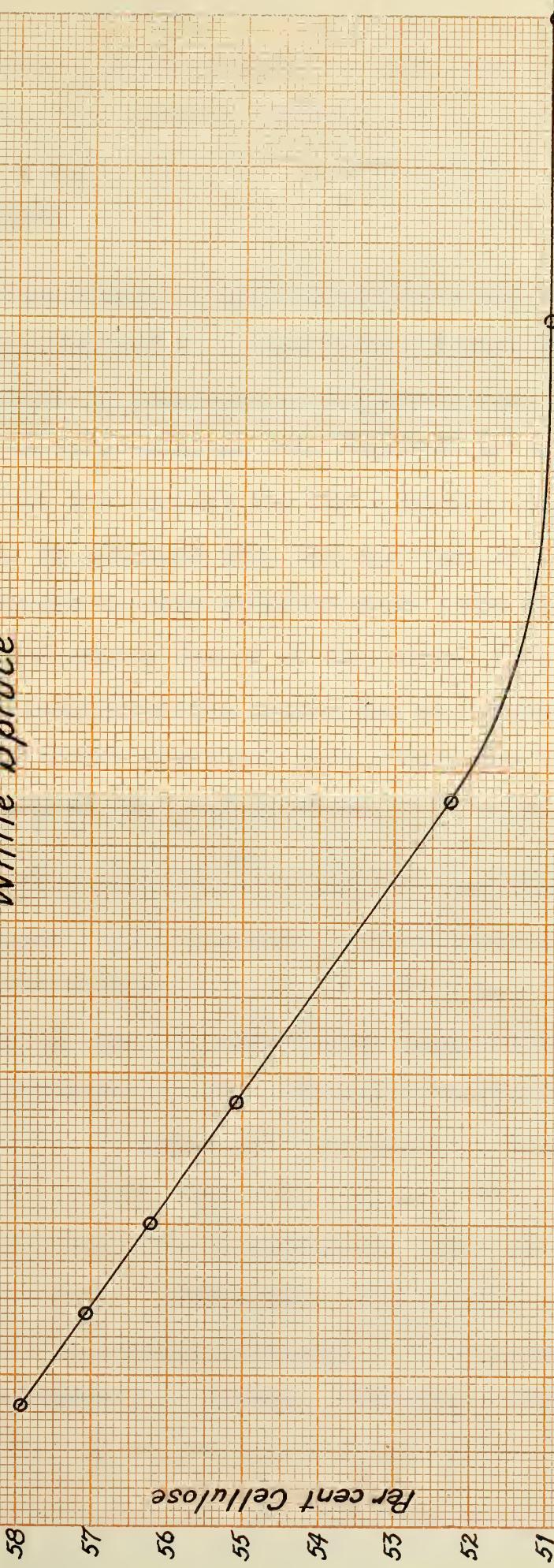
Per cent Cellulose

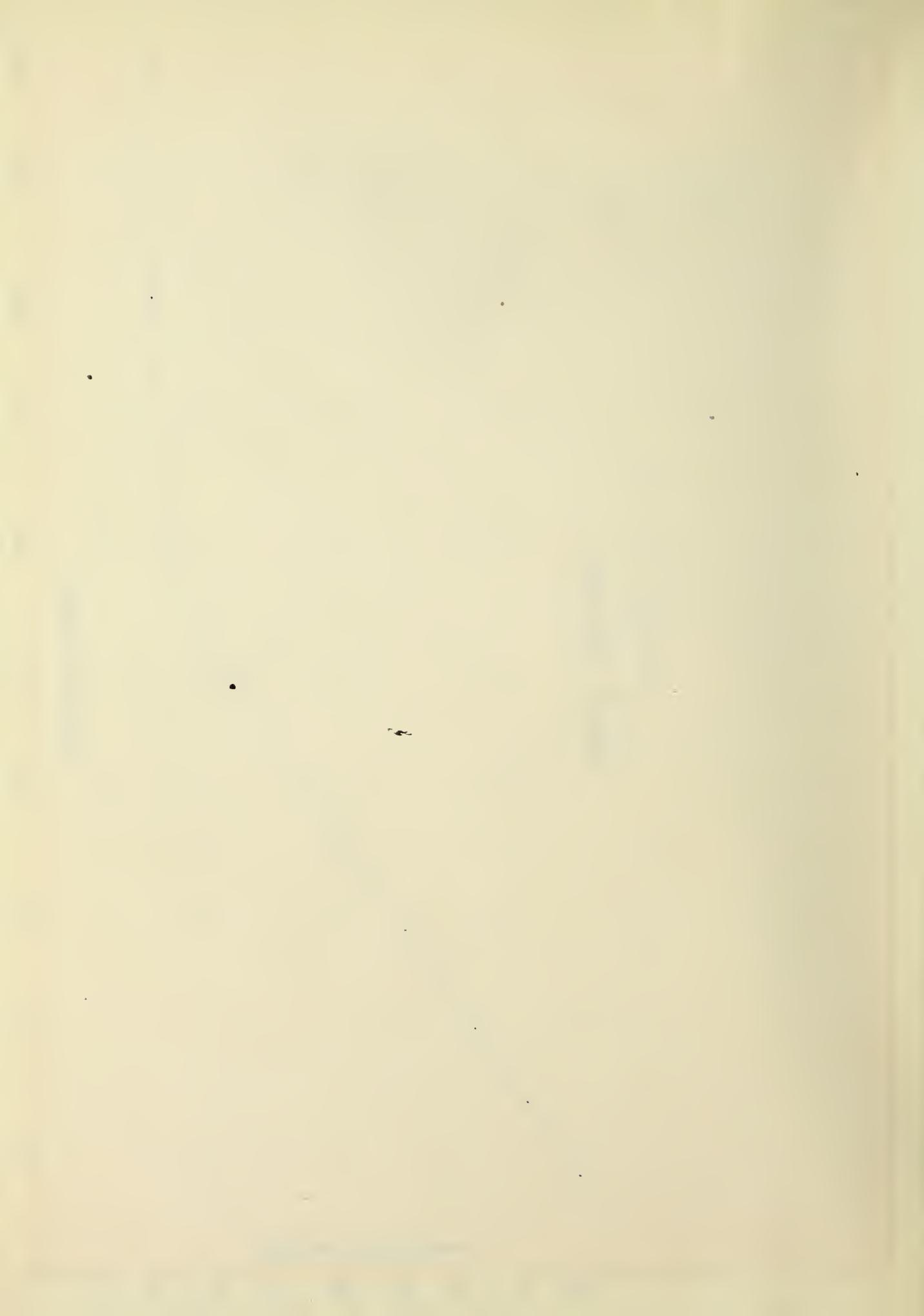
58 57 56 55 54 53 52 51 50

100
90
80
70
60
50
40
30
20
10

0

Degree of Mesh





No conclusions could be made from the results of the cellulose determination in the Hemlock because, due to some inconsistency in the sample, results could not be obtained that would check within a reasonable margin.

Plotting the degree of mesh as abscissa and the per cent of cellulose as ordinates, curves 1, 2, and 3 were drawn. It is evident from these curves that the per cent of cellulose varies with the mesh according to some certain equation (the equation of the curve). Assuming that these curves are correct for White Spruce, Balsam, and Poplar, it seems logical to conclude that the per cent of cellulose of any mesh could be changed to some standard mesh - for instance 80 mesh - by applying the correction factor of the curve. This would not aid in obtaining a more representative sample but it certainly would render the results of different operators more comparable than they are under the methods used at the present time.

It is to be noted in Curve 1 that the per cent of cellulose is in a steady decrease from 8 to 50 or 60 mesh and from there on it is practically constant. It is for that reason that most modern methods recommend the use of sawdust that passes through an 80 mesh screen but is retained on a 100 mesh sieve. Never-the-less, a sample of that size is not representative of the entire portion of sawdust (see Table 1). It is true that a portion of the 8 or 14 mesh size is too large because, in order to remove all the lignin from the larger particles, the entire sample must be subjected to such a long chlorination that the smaller particles will be oxidized to oxy-celluloses which are soluble in Na_2SO_3 . According to the curve the per cent of lignin removed in proportion to the entire sample

100

90

80

70

60

50

40

30

20

10

0

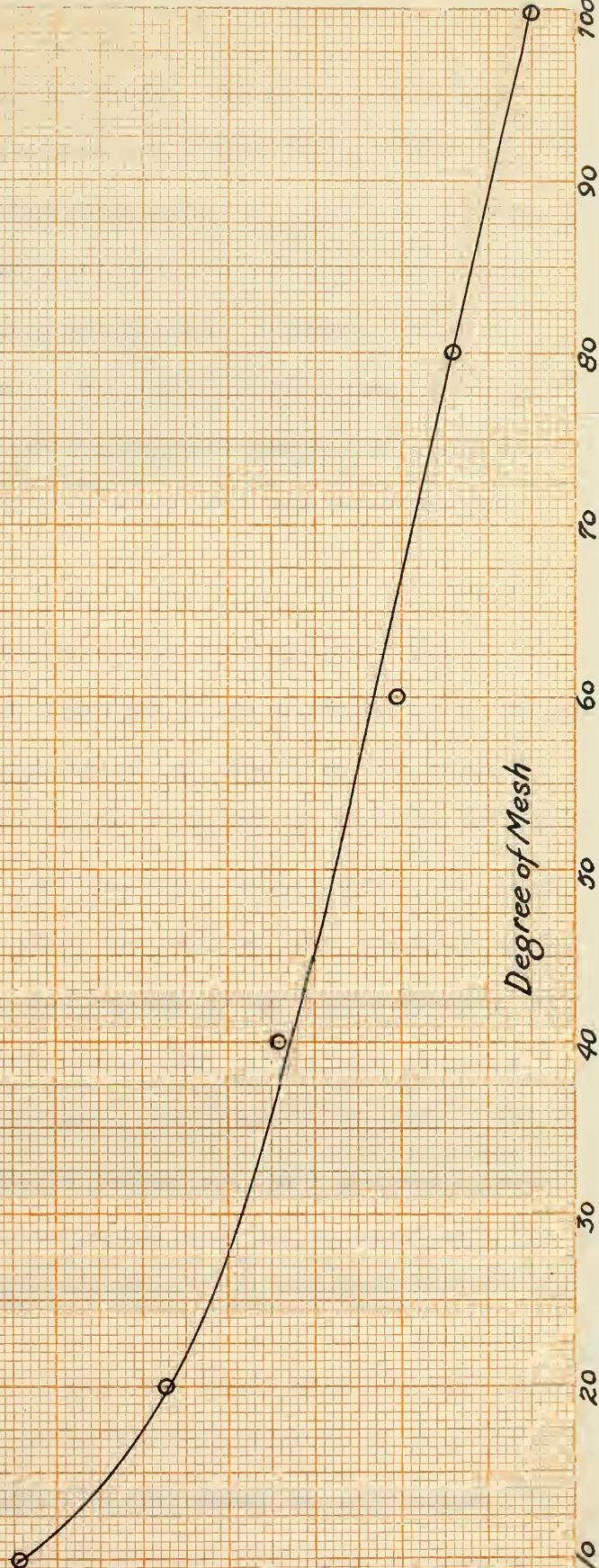
Per cent Cellulose

52 51 50 49 48 47 46 45

Curve 2
Balsam

Curve 2

Balsam



increases to some point between 50 or 60 mesh . At this place some change evidently takes place which, as yet, has not been investigated but it is probably o point representing the size of particle which is of such a small and uniform size that more or all of the lignin is removed in the same time a smaller percentage was removed in the larger meshes. At the same time it must be remembered that, even with the larger meshes, the chlorination was continued until the addition of Na_2SO_3 solution to the sawdust did not give the characteristic color of lignin derivatives.

Considering these two conflicting statements, the questions arise: Is all of the lignin removed from sawdust of a large mesh (10-20)? Why is not the cellulose value of the 8 or 10 mesh portion just as representative of the entire sample as is the 80 -100 mesh? If all the lignin is^{not} removed, the residue should give the characteristic color with chlorine and Na_2SO_3 but all of the samples were chlorinated to a point where further chlorination or the addition of Na_2SO_3 solution produced no color. But since the cellulose content decreases steadily from 8 to 50 or 60 mesh, it seeme reasonable to beleive that something besides lignin is being removed between those margins or else the less resistant celluloses are being oxidized to substances that are soluble in Na_2SO_3 .

Curve 2, that of Balsam, does not have exactly the same shape as doed the one for White Spruce probably because of the inherent characteristics of the two woods. The decrease in cellulose content with the decrease in mesh is much slower and does not come to such a constant value as does the White Spruce, although the percentages of the 80 and 100 mesh portions of Balsam are not more than

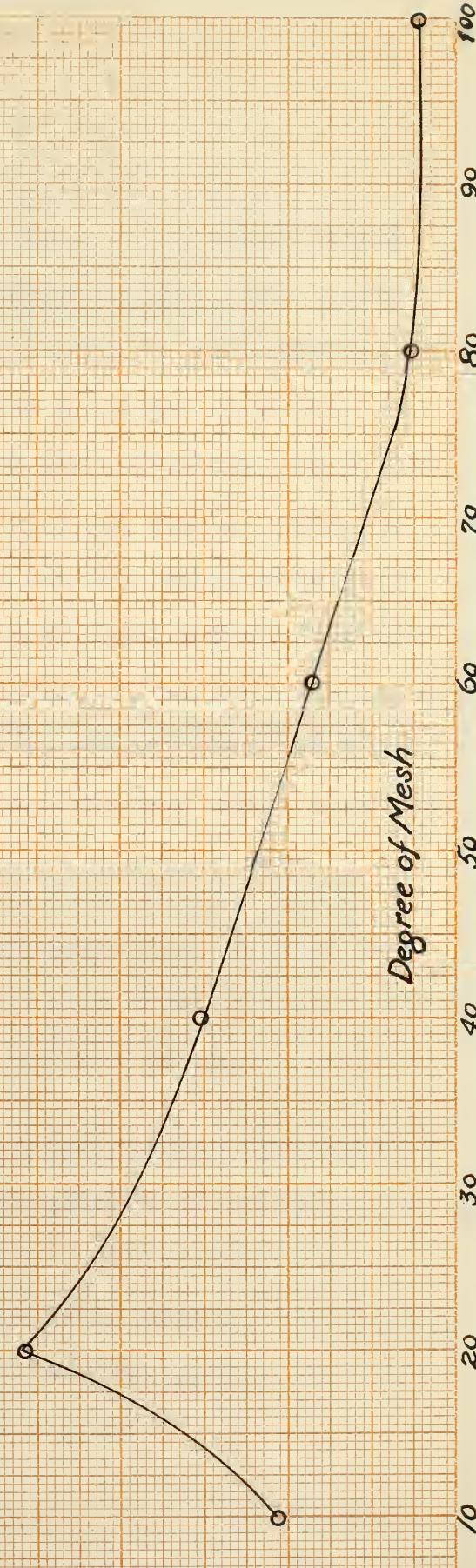
Per cent Cellulose

60 59 58 57 56 55 54

Curve 3
Poplar

Degree of Mesh

100 90 80 70 60 50 40 30 20 10



1% apart.

Curve 3, that of Poplar, is practically the same as that of White Spruce except for the peak that occurs at 20 mesh instead of 10. A possible explanation for that feature is that, due to the fibrous character and nonuniformity of the sample between the meshes of 10 and 20, the sample of 10 mesh required a longer chlorination period than others and consequently more of the cellulose would have destroyed in order to produce a residue free from lignin. Then the sample of 20 mesh, being more uniform than the 10, would require a shorter time for chlorination and consequently less cellulose would be oxidized to oxy-celluloses or other compounds that are soluble in Na_2SO_3 solution. The other part of curve 3 is practically the same as curve 1, the cellulose content decreasing steadily until about 60 or 70 mesh where the cellulose value reaches a constant mark.

Cellulose determinations were also run on Hemlock but because results could not be obtained that would check within a reasonable margin the curve for that wood was not drawn.

Throughout the discussion of these results the "cellulose content" or "cellulose value" will be referred to as being the per cent of residue from the original sample - the residue being obtained by successive alternate treatments with chlorine and Na_2SO_3 solution until free from lignin but without any correction for the pentosan or methyl pentosan content of the residue.

It is regretted that the residues after each chlorination could not be analyzed for, if such data was compiled with that already collected during this work, a more thorough and accurate explanation of the curves would be possible. However, in each case it is very

evident that, although all of the lignin was removed in each case, the cellulose content decreased with the decrease in size of particle in all woods that were used in this work.

Mahood's conclusion (4) that "the material which passes through an 80 mesh screen and is retained on a 100 mesh screen is the most satisfactory for cellulose determinations", is correct. Such a sample is the most satisfactory in that it requires shorter periods of chlorination; but to take such a sample as being representative of the entire quantity of sawdust sampled when the results of this investigation show that coarser sawdust is just as free from lignin but has higher cellulose values than the smaller sawdust, does not appear to be justifiable. Conclusions as to the correct mesh of sawdust to use in cellulose determinations can be made only after the exact composition of "wood cellulose" and the residues after each chlorination are known. Such conclusions must await the results of the investigators of today who are attempting to establish a complete and accurate knowledge of the chemistry of wood cellulose and until such facts are known, paper mills and other industries using cellulose determinations should use considerable discretion in the method used.

Summary

1. The previous work on the subject of "Determination of Cellulose in Wood" has been reviewed.
2. The cellulose content of White Spruce, Balsam, Poplar and Hemlock has been determined by the Cross and Bevan method using samples of at least six different meshes varying in size from 10 to 100 mesh.
3. Curves for the woods used have been drawn, plotting the degree of mesh against the cellulose content of the wood at that mesh.
4. From the experimental work compiled during this investigation it seems justifiable to conclude that the curves for White Spruce, Balsam, and Hemlock, plotting the degree of mesh against the per cent cellulose at that mesh, afford a means of comparing the results of cellulose determinations from different operators who use procedures involving the use of sawdust of various sizes.

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